RESEARCH ARTICLES

J. Sci. Soc. Thailand, **6** (1980) 178-182

OPTIMIZED GAUSSIAN EXPANSION OF ATOMIC ORBITALS

SIRIRAT HO-AMPAWANWONG

Department of Chemistry, Faculty of Science, Chulalongkorn University, Phya Thai Rd., Bangkok, Thailand

(Received 2 September 1980)

Summary

Property-optimized Gaussian expansions of Slater-type orbitals (STO) were used to calculate the ground state energy and the one-electron molecular properties of the water molecule and the NH_2^- *species. The effect of simultaneously using a weighting factor and pseudonormalization was studied. The weighting factor was seen to give a definite improvement: in the energy calculation, the weighting factor* r^{-1} *gives satisfactory results, i.e. the energy is improved by about 0.7 a.u. (from −72.78278 a.u. to −73.52642 a.u.) compared to the unweighted expansion with STO−2G for the water molecule (at a bond angle of 105°). The weighting factor* r^1 *gives an extremely good result in the dipole moment calculation. For the water molecule with STO−2G it is 0.5633 a.u. while the unweighted fitting gives 0.4954 a.u. compared to the STO result of 0.5642 a.u.*

Introduction

Replacement of each Slater-type orbital (STO) with a linear combination of Gaussian-type orbitals (GTO's) is used extensively because of the simplicity of the evaluation of the molecular integrals over GTO's. The usual approach[1,2] is to use an unweighted expansion over the whole range of interest, but since the approximations are, for economy, small term expansions, the fit in some regions is poorer than in others, resulting in poor expectation values for properties that depend on the former regions.

To improve the fittings for specific regions in space, the weighting factor w(r) was introduced[3, 4] in the minimization of the error expression

$$\varepsilon = \int_0^\infty [S(r) - \sum_{i=1}^{N} d_i G_i(r)]^2 \, w(r) \, dr$$

where $S(r)$ = the radial part of a STO
and $G(r)$ = the radial part of a GTO

Many expectation values are greatly improved in small term expansions when weighting factors proportional to the radial dependence of the operator are utilized. While Page and Ludwig[3] concentrated on the improvement of individual integrals, the present work looks at the improvement to be gained in the context of a complete calculation on a non-trivial molecule.

The water molecule and the NH_2^- ion are used in this work to study the effect of such weighting factors upon the energy and one-electron molecular properties. The calculations of Ellison and Shull[5] on water were repeated; for the NH_2^- ion, Bell's optimum geometry[6] was used.

The weighted expansions reported by Page and Ludwig[3] are not strictly normalized, since forcing normalization would require that the fit be good in two different regions simultaneously, weighted for r^k and for $r^o = 1$ respectively. The pseudonormalization techniques[3, 4] whereby unnormalized expectation values are divided by the expectation value of unity calculated with an r^o-weighted expansion of equal length is introduced into the calculations to provide better space-filling properties in the region sampled. Thus we replace $\phi\,(r_A)$ (STO at center A) by a linear combination of GTO, $E_N^k\,(r_A)$, an expansion of N terms obtained using a weighting of r^k (where $k = 0$ for the overlap integrals).

$$E_N^k\,(r_A) = \sum_{i=1}^{N} d_i G_i\,(r_A), \text{ then we take e.g.}$$

$$\int \phi_A \text{ op } \phi_B dV = \frac{\int E_N^k\,(r_A) \text{ op } E_N^k\,(r_B)\, dV}{[\int \left\{E_N^k\,(r_A)\right\}^2 dV . \int \left\{E_N^k\,(r_B)\right\}^2 dV]^{1/2}}$$

Energy Calculations

The inclusion of the weighting factor gives very satisfactory results compared to the unweighted expansion, especially in the small term ($N = 2$ or 3) expansions (called STO-NG).

A choice of r^{-1} weighting gives a fit to the STO that is better in the small r region and is comparable to the unweighted expansion in the intermediate region. This improves the STO–2G energy of the water molecule by about 0.7 a.u. and that of the NH_2^- ion by about 0.5 a.u. compared to the unweighted results (Table 1). With the optimum geometry and STO–4G. People[7] obtained –75.500013 a.u. for the ground state energy of the water molecule while a r^{-1} weighted STO–4G expansion gives an energy –75.59530 a.u.

TABLE 1. THE GROUND STATE ENERGY OF THE WATER MOLECULE AND THE NH_2^- ION (IN a.u.)

	H_2O		NH_2^-	
w(r)	r^o	r^{-1}	r^o	r^{-1}
STO–2G	–72.78278	–73.52632	–53.00271	–53.51651
STO–3G	–74.90463	–75.19923	–54.58839	–54.81112
STO–4G	–75.43351	–75.54523	–54.98853	–55.07197
STO–6G	–75.63124	–75.64716	–55.13883	–55.15100
STO (ref. 8):	–75.65560			

It is interesting to note that the difference between the Gaussian expansion energy and the STO energy for varying bond angles is relatively constant when using as weighting factor either r^{-1} or r^o (Table 2)

TABLE 2. GTO EXPANSIONS AND THE STO ENERGY OF THE WATER MOLECULE (IN HARTREES) AT DIFFERENT BOND ANGLES

H-O-H	STO-2G(r^o)	STO-2G(r^{-1})	STO(7)	△[STO-2G(r^o)-STO]	△[STO-2G(r^{-1})-STO]
90	–72.78048	–73.52488	–75.65249	2.87201	2.12761
95	–72.78382	–73.52807	–75.65589	2.87207	2.12782
100	–72.78450	–73.52849	–75.65684	2.87234	2.12835
105	–72.78278	–73.52642	–75.65560	2.87282	2.12918
110	–72.77898	–73.52211	–75.65239	2.87341	2.13028
120	–72.76579	–73.50765	–75.64096	2.87517	2.13331
180	–72.66058	–73.38572	–75.54717	2.88659	2.16145

The results on several one-electron molecular properties show that the use of the 'reasonable' weighting factor and pseudonormalization improve the values considerably.

With the weighting factor r^{+1}, the convergence of dipole moment is extremely good, and no oscillation is observed as N increases. In STO–2G, the difference from STO for the water molecule is about 0.003 debye. To get an equally good result without weighting, an expansion length of at least four has to be used (cf. Table 3)

TABLE 3. THE DIPOLE MOMENT OF THE WATER MOLECULE AND THE NH_2^- ION (IN DEBYE, 1 a.u. = 2.54 DEBYE)

	H_2O		NH_2^- [a]	
w(r)	r^{+1}	r^o	r^{+1}	r^o
STO–2G	1.4308	1.2583	–0.2117	–0.3422
STO–3G	1.4243	1.3926	–0.2814	–0.3132
STO–4G	1.4273	1.4321	–0.2959	–0.2802
STO–6G	1.4332	1.4346	–0.2864	–0.2846
STO (ref. 8):	1.4322			

[a] N is at the origin

According to ref. 3, the weighting factor is expected to be the same as the radial dependence of the operator used. This is found for the dipole moment results but not for $<r^2>$. A smaller oscillation of the values is observed when r^{+1} weighting is used. The values of $<r^2>$ are shown in Table 4

TABLE 4. $<r^2>$ FOR THE WATER MOLECULE RELATIVE TO THE CENTER OF MASS (IN 10^{-16} cm^2)

w(r)	r^{+2}	r^{+1}	r^o	
STO-2G	4.9742	5.4430	5.5193	
STO-3G	5.3109	5.4101	5.4209	
STO-4G	5.3800	5.4046	5.4059	
STO-6G	5.4007	5.4030	5.4033	5.462[a]

[a] this value was calculate using 26 basis function[9]

Properties Near The Origin

It is a widely held belief that a GTO expansion for s-type functions is unsuitable for properties which depend on the wave function value at a nucleus, since such functions cannot satisfy the cusp condition. Yurtsever and Hinze[10] showed that this is not necessarily true. They did not, however, show that such properties may be obtained readily or reliably.

When the weighting factor r^{-1} and pseudonormalization are used in the calculation of the electron density at the nuclei, the STO-2G value yields 65% of the STO value at the oxygen and 78% at the hydrogen nuclei, while the unweighted expansion gives 47% and 61%, respectively. These results are even better than those given by the unweighted STO-3G expansion.

The results for the electron density at the intermediate r region, e.g. at the OH midpoint and at the OH center of charge are more sensitive to the size of the Gaussian expansion than to the choice of weighting factor. All the values are close to the STO values when four Gaussians are used.

The electron density at a distance far from the nuclei, e.g. at a point corresponding to the position of Li^+ in H_2O-Li^+, is of course very small (on the order of 10^{-5} to 10^{-6} a.u.). The weighting factor r^{+2} improves the STO-3G electron density from 75% of the STO result to 102% the STO result compared with the unweighted expansion.

Conclusions

From the study of the effect of weighting factors and of pseudonormalization on the energy and one electron properties, we suggest that:

1. Psuedonormalization should be used in all calculations.

2. For any property involving a small distance, e.g. energy and electron density at the nuclei, the weithging factor r^{-1} should be used.

3. For the properties involving a large distance, the weighting factor r^{+1} should be used.

4. In dipole moment calculations, the weighting factor r^{+1} should give very satisfactory results.

5. For properties involving an intermediate distance, the size of the Gaussian expansion seems to be more important than the choice of the weighting factor.

References

1. O-Ohata, K., Taketa, H. and Huzinaga, S. (1966) *J. Phys. Soc. Japan* **21**, 2306.
2. Hehre, W.J., Stewart, R.F. and Pople, J.A. (1969) *J. Chem. Phys.* **51**, 2657.
3. Page, G. and Ludwig, O.G. (1972) *J. Chem. Phys.* **56**, 5626.
4. Page, G. (1973) Doctoral Thesis, Villanova University.
5. Elllion, F.O. and Shull, H. (1955) *J. Chem. Phys.* **23**, 2348.
6. Bell, S. (1978) *J. Chem. Phys.* **69**, 3879.
7. Del Bene, J. and Pople, J.A. (1970) *J. Chem. Phys.* **52**, 4858.
8. Pitzer, R.M. and Merrifield, D.P. (1970) *J. Chem. Phys.* **52**, 4782.
9. Aung, S. Pitzer, R.M. and Chan S. (1968) *J. Chem. Phys.* **49**, 2071.
10. Yurtsever, E. and Hinze, J. (1978) *J. Chem. Phys.* **69**, 3431.

บทคัดย่อ

ในการคำนวณหาพลังงานที่สถานะพื้น และคุณสมบัติบางอย่างของโมเลกุลของน้ำ และ NH_2^- ได้ใช้การกระจายของเกาส์เซียนที่ออพทิไมซ์ แทนวงโคจรแบบสเลเตอร์ (STO) และได้ทำการศึกษาถึงอิทธิพลของการใช้เวททิงแฟคเตอร์ และซูโดนอร์มอไลเซชันพร้อม ๆ กัน เวททิงแฟคเตอร์ทำให้พลังงานที่คำนวณได้ดีขึ้นกว่าที่ไม่ใช้เวททิงแฟคเตอร์ กล่าวคือ เวททิงแฟคเตอร์ r^{-1} ทำให้พลังงานของน้ำที่มีมุมระหว่างพันธะเป็น 105° เมื่อใช้ STO–2G ดีขึ้นถึง 0.7 a.u. (คือจาก -72.78278 a.u. เป็น -73.52642 a.u.) ส่วนเวททิงแฟคเตอร์ r^1 ให้ค่าของไดโพลโมเมนท์ดีมาก คือในโมเลกุลของน้ำ เมื่อใช้ STO–2G จะได้ค่า 0.5633 a.u. ขณะที่ไดโพลโมเมนท์ที่คำนวณโดยไม่ใช้เวททิงแฟคเตอร์ได้ 0.4954 a.u. เปรียบเทียบกับผลที่ได้จาก STO ซึ่งมีค่า 0.5642 a.u.